

## PREPARATION AND PROPERTIES OF GREEN RUST TYPE SUBSTANCES

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A method has been worked out for the reproducible preparation of Green Rust substances involving  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  anions. The chemical composition of the substances prepared has been followed in dependence on the synthesis conditions. The powder X-ray and electron diffraction patterns and infrared and Moessbauer spectra have been measured and discussed.

Oxidation of aqueous solutions of  $\text{Fe}^{2+}$  salts by air oxygen at  $\text{pH} > 6$  involves the formation of intermediate blue-green precipitates containing both iron(II) and iron(III) and the anion of the starting iron(II) salt. In the literature these substances are referred to as Green Rust (GR).

The first to give a detailed description of these substances were Keller and Feitknecht<sup>1</sup>, who examined the oxidation of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})\text{Cl}$  by air oxygen in aqueous solutions containing  $\text{NH}_4\text{Cl}$ . The authors suggest that the composition of the GR precipitate is  $3 \text{Fe}(\text{OH})_2 \cdot \text{FeOCl} \cdot x\text{H}_2\text{O}$ . Bernal and coworkers<sup>2</sup> discriminate two types of GR, referring to them as GR I and GR II; the two types differ in their crystal symmetry, GR I being rhombohedral and GR II, hexagonal. The authors suppose that GR II is an oxidation product of GR I. More recently, it was observed<sup>3,4</sup> that GR I and GR II only form in solutions containing  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions, respectively. The formation of GR was also observed during the corrosion or anodic oxidation of iron metal<sup>2,5</sup>.

The preparation of GR precipitates in a defined state is hampered by the fact that iron(II) in them is oxidized readily and the precipitate itself is thermally not very stable. Their decomposition results in  $\text{Fe}_3\text{O}_4$ , their oxidation by air oxygen gives rise to iron(III) oxide-hydroxides<sup>6</sup>. GR are stabilized by anions, particularly  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , which, however, are not bound in them very strongly; washed with water, the precipitate exchanges these ions readily for  $\text{OH}^-$  ions by which it is not stabilized<sup>2,4,7</sup>.

Feitknecht<sup>8</sup> and Allman<sup>9</sup> suggest that Green Rust is a particular case of mixed hydroxides possessing the pyroaurite-sjögrenite structure. This structure is constituted by a planar layer of octahedra, the centres of which accommodate atoms of the metal and the corners,  $\text{OH}^-$  groups. The structure of this layer is identical with that of layers in the crystal lattice of hydroxides of some divalent metals such as

$\text{Fe}(\text{OH})_2$  or  $\text{Ni}(\text{OH})_2$ . A fraction of the divalent metal ions is substituted by the trivalent metal ions in the GR precipitate, the positive charge being compensated for by an anion layer ( $\text{CO}_3^{2-}$  in pyroaurite). The hydroxide and anion layers alternate regularly. The symmetry of the crystal lattice depends on the mutual displacement of the layers. If identical positions repeat in every layer or every other layer, the symmetry is hexagonal, if it repeats in every third layer, the symmetry is rhombohedral.

It is a prerequisite for their study that a procedure for a reproducible preparation of these substances in a sufficiently stable state be available. Such a procedure is described in this paper; the precipitates prepared, involving various anions, are characterized by several physico-chemical methods.

## EXPERIMENTAL

### Apparatus and Procedure

The layout of the apparatus used is shown in Fig. 1. Stock solution of iron(II) salt was prepared in vessel A.  $\text{Fe}^{3+}$  impurities were reduced with excess iron metal powder for two days, the solution was filtered through filter B into vessel C. From this vessel the solution was transferred to the reaction vessel D prior to the oxidation.

The reaction vessel, with a useful volume of  $500 \text{ cm}^3$ , was fitted with a thermostating water jacket. The right section of the vessel ( $D_2$ ) accommodated an Ultra Turrax stirrer (G); argon (ar) or air could be fed in through inlet H. The air flow rate was measured with a capillary flow

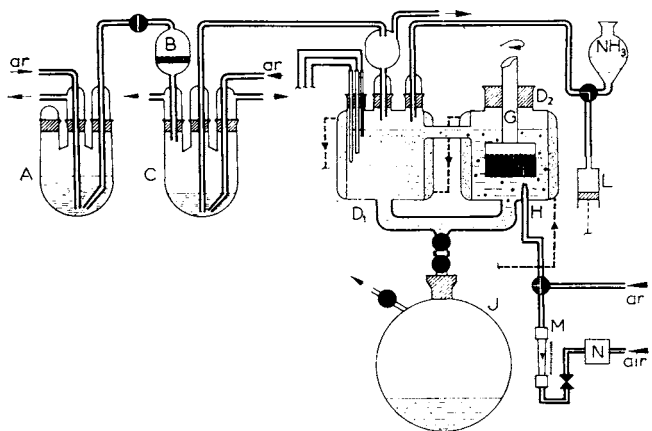


FIG. 1

Layout of the apparatus used. A,  $D_1$ ,  $D_2$  reaction vessels, B filter, C stock solution container, G dispersing stirrer, H inlets, J vessel for product isolation, L automatic burette, M capillary flow meter, N liquid manostat

meter M and stabilized with a liquid manostat N. The left section of the reaction vessel ( $D_1$ ) accommodated a combined glass electrode interfaced to a TTT-1 pH-stat (Radiometer, Copenhagen), which controlled the automatic burette L by means of which a 25% aqueous solution of  $NH_3$  was added. In this manner the pH could be held constant to within  $\pm 0.05$  during the oxidation. The  $D_1$  section also accommodated a Vertex contact thermometer for controlling the temperature of water in the jacket by means of a Hoepler thermostat.

The iron(II) salt solution was fed to the reaction vessel and the stirring was activated; in this manner an efficient dispersion of the gas and circulation of the solution through the vessel were ensured. The pH was adjusted under argon and held constant during the experiment. The oxidation was commenced by replacing the argon stream with air. Owing to the hydrolysis processes the solution becomes acidic; ammonia was therefore added in order to maintain the pH constant. The ammonia consumption was recorded as a function of time throughout the experiment. In a preselected time the oxidation was discontinued by replacing the air stream by argon and the suspension was drained into vessel J containing  $250\text{ cm}^3$  of methanol. The vessel was disconnected from the apparatus and transferred to a polyethylene glove bag with inert argon atmosphere. The suspension was filtered out and washed with  $500\text{ cm}^3$  of methanol and  $500\text{ cm}^3$  of ether. The preparation was dried at  $20^\circ\text{C}$  in the vacuum of an oil pump, and added to measuring cells or to glass vessels with double ground joints under inert atmosphere. Methanol was chosen for washing because washed with water, GR liberates anions and the product then is often contaminated by decomposition products (magnetite, iron(III) oxide-hydroxides).

#### Chemicals

Aqueous solutions of iron(II) sulphate, chloride, bromide, iodide and perchlorate were prepared by dissolving iron metal in the respective acids at room temperature (iron perchlorate, at  $0^\circ\text{C}$ ). Iron(II) nitrate was prepared by reacting  $Pb(NO_3)_2$  with  $FeSO_4$  in water.

Sulphuric acid 98%, hydrochloric acid 35%, hydrobromic acid 55%, and perchloric acid 70% as well as aqueous ammonia 25% and lead nitrate were reagent grade chemicals supplied by Lachema, Brno; hydroiodic acid of reagent grade purity was obtained from Merck, Darmstadt. Reduced iron powder, Mn content 0.05%, was also obtained from Lachema, Brno.

#### Physical Methods

Powder X-ray diffraction patterns were obtained on a DRON 2-0. diffractometer (Burevestnik + Leningrad) using  $CoK_\alpha$  radiation. The samples were accommodated in organic glass cells coated with a Myllard foil. The foil prevented the sample from oxidation during the measurement; diffraction lines corresponding to interplanar distances of 3.15–3.83 nm, however, could not be measured.

Infrared spectra were scanned on a Beckman IR-20 A grating spectrophotometer over the  $250\text{--}4000\text{ cm}^{-1}$  region. The samples were measured as 5% Nujol and 15% perfluorokerosene mulls.

Moessbauer spectra were run on a 512-channel spectrometer with a constant acceleration (KFKI, Budapest) using a  $^{67}\text{Co}$  source in a Rh matrix. The samples were sealed in poly(methyl methacrylate) cells.

Microphotographs and electron diffraction patterns of the iron(II) salt oxidation intermediates were obtained on a Tesla 242 E transmission electron microscope. Sample suspensions were taken with a syringe directly from the reaction vessel, applied to a grid with a Formvar foil in an inert atmosphere, washed with a drop of water, and dried in a vacuum of the electron microscope. Polycrystalline gold, applied to the foil beside each sample, served as the standard.

The chemical composition of the product was determined for samples sealed in glass ampoules. The ampoule was broken in 0.1M-H<sub>2</sub>SO<sub>4</sub> under argon. Iron(II) ions were determined manganometrically, the sample was reduced, and total iron was determined. The remaining components were determined in sample oxidized in air; iron was also determined in this sample and the concentrations of the components were converted to those for the unoxidized sample.

## RESULTS AND DISCUSSION

Fig. 2 shows the time dependence of takeup of the neutralizing agent during the oxidation of iron(II) oxide precipitate at a constant pH. The oxidation rate can be controlled *via* the air flow rate; up to a volumetric flow rate of about 1 min<sup>-1</sup>, all oxygen is taken up and the oxidation rate is thus proportional to the rate of air flow through the suspension. The arrows in Fig. 2 indicate the region where the oxidation is associated with no consumption of the neutralizing agent. In this region the suspension is constituted by GR precipitate. The properties of the precipitate depend on the synthesis conditions. Our experiments suggest the following optimum conditions for the preparation of pure GR.

The preparation of phase-pure GR requires that pH be held within the range of 7–7.5; iron(III) oxide-hydroxides are then absent, the precipitate has best-developed crystal structure, constituted by a unique type of particles. At higher pH an amorphous impurity is present, at lower pH goethite appears frequently.

The optimum temperature for the synthesis is 20–25°C. At higher temperatures the precipitate decomposes partly to magnetite, at lower temperatures amorphous components are present.

The volumetric air flow rate of 0.25 min<sup>-1</sup> was chosen for the experiments, the concentration of Fe<sup>2+</sup> was 20 g l<sup>-1</sup>. Variations in these parameters do not affect the properties of the product appreciably; the values used followed from the actual experimental arrangement (sampling, sample handling, amount of sample).

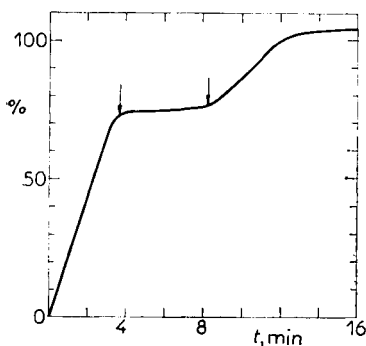
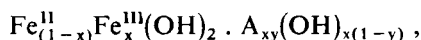


FIG. 2  
Time dependence of ammonia takeup during the preparation of GR

In this way, GR substances were prepared from iron(II) sulphate, chloride, bromide, and iodide. Iron(II) perchlorate afforded GR which was very little stable, decomposing readily to  $\text{Fe}_3\text{O}_4$ . Attempted isolation failed even at  $0^\circ\text{C}$ . Iron(II) nitrate did not give rise to a pure GR either because iron(II) in the GR was oxidized by the nitrate ions.

The chemical composition of the GR precipitates obtained can be represented by the formula



where  $x = (0.4-0.7)$ ,  $y = (0.3-0.5)$ .  $\text{A} = 1/2\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ . The composition of the GR is variable, the  $\text{Fe}^{3+}$  content increases during the oxidation, and at  $x = 0.7$  the GR oxidizes to  $\gamma\text{-FeOOH}$ . It can be inferred from the formula that within the region of  $x$  corresponding to the occurrence of the GR precipitate, hydrolytic liberation of  $\text{OH}^-$  ions does not occur during the oxidation. This is the reason for the step-shaped time dependence of the neutralizing agent takeup (Fig. 2). No takeup of this agent was observed for  $x = 0.4-0.7$ . The total anion content of GR depends on the anion concentration in the solution and pH; the anion content decreases with increasing pH. At low anion contents the GR is unstable, decomposing to magnetite. Thus, GR is stabilized by enhanced anion concentrations in solution and by low pH.

The Miller index assignment to the powder X-ray diffraction patterns of GR is given in Table I. The results are consistent with published data<sup>1,2,10</sup>. GR- $\text{SO}_4$  belongs to the hexagonal system, GR-Cl, Gr-Br, and GR-I, to the rhombohedral system (hexagonal R type). The structure of the halide GR is identical with that referred to<sup>2</sup> as GR I. The results do not disagree with the concept of the structure of GR substances being identical with the pyroaurite structure. The elementary cell consists of three  $\text{Fe}(\text{OH})_2^{\text{n}+}$  layers and three layers of anions. The type of the layer structure of GR substances is also confirmed by the dependence of the lattice parameters on the anion size (Fig. 3). Parameter  $a$  of the hexagonal lattice is virtually independent of the anion type, whereas parameter  $c$  increases linearly with the anion radius.

GR- $\text{SO}_4$  is identical with the substance referred to as GR II. The different hexagonal symmetry of the lattice is a consequence of the different mutual displacement of the  $\text{Fe}(\text{OH})_2^{\text{n}+}$  layers. The elementary cell of GR- $\text{SO}_4$  is constituted by a single layer of  $\text{Fe}(\text{OH})_2^{\text{n}+}$  and a single layer of anions. The difference between the two types of GR is probably due to the different shape of the anions and perhaps also to the occurrence of directed bonds such as hydrogen bridges. Conversion of GR I to GR II or *vice versa* was never observed during the oxidation unless anions were also replaced.

The microphotographs of GR revealed crystal platelets 0.5  $\mu\text{m}$  in size. Electron diffraction patterns were also obtained; their evaluation is given in Tables II and III. The data confirm the conclusions following from the X-ray diffraction patterns.

The infrared spectra of GR display characteristic bands whose positions are given in Table IV. The band pair at 670–720  $\text{cm}^{-1}$  is probably due to the O—Fe—A stretching vibration (A = anion). The band positions exhibit shifts in dependence

TABLE I  
Evaluation of powder X-ray diffraction patterns of Green Rust compounds with different anions

$\text{SO}_4^{2-}$					$h$ $k$ $l$			$\text{Cl}^-$		$\text{Br}^-$		$\text{I}^-$	
$h$	$k$	$l$	$d$ nm	$I$ %				$d$ nm	$I$ %	$d$ nm	$I$ %	$d$ nm	$I$ %
0	0	1	1.12	80	0	0	3	0.793	90	0.797	80	0.829	20
0	0	2	0.558	40	0	0	6	0.379	100	0.397	100	0.414	100
0	0	3	0.377	100	1	0	1	0.276	5	0.275	5	0.275	
1	0	0	0.276	20	0	0	9	—	—	0.269		0.275	5
1	0	1	0.269	20	0	1	2	0.271	50	0.269	60	0.270	5
1	0	2	0.248	40	0	1	5	0.240	10	0.239	40	0.245	20
1	0	3	0.222	5	0	1	8	0.203	10	—	—	—	—
1	0	4	0.194	5	2	1	1	0.160	30	—	—	—	—
1	0	5	0.174	5	1	1	0	—	—	0.159	20	0.160	5
1	1	0	0.159	10	1	1	3	0.157	10	0.157	20	0.157	5
1	1	1	0.158	10	0	0	18	0.132	5	—	—	—	—
1	1	2	0.153	5									
1	1	3	0.146	5									

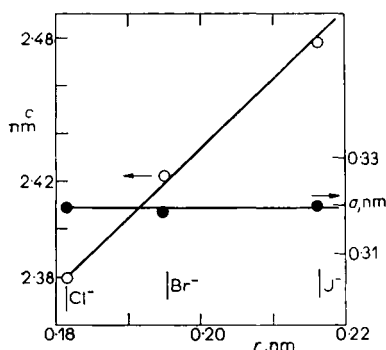


FIG. 3  
Dependence of lattice parameters  $a$  ● and  $c$  ○ on the size of anion in the GR lattice

TABLE II

Evaluation of electron diffraction patterns of the intermediate products of oxidation of  $\text{FeSO}_4$  at pH 7.5 in dependence on the oxidation time

3 min oxidation			4 min oxidation			6 min oxidation			8 min oxidation			12 min oxidation		
<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>
0.263	90	GR	0.347	10	L	0.328	40	L	0.324	40	L	0.340	5	L
0.187	10	GR	0.269	90	GR	0.268	30	GR	0.203	15	L	0.239	20	L
0.151	100	GR	0.240	5	L	0.244	15	L	0.192	100	L	0.196	100	L
0.131	10	GR	0.191	20	L	0.231	15	L	0.151	70	L	0.155	80	L
0.099	5	GR	0.154	100	L + GR	0.189	100	LG	0.147	15	L	0.141	5	L
0.088	5	GR	0.134	5	GR	0.153	50	L	0.119	50	L	0.121	50	L
			0.119	10	L	0.148	90	L + GR	0.097	5	L	0.099	5	L
			0.100	5	L + GR	0.138	15	L				0.083	5	L
			0.090	5	L + GR	0.118	50	L						
						0.096	5	L + GR						

<sup>a</sup> GR = Green Rust, L = lepidocrocite ( $\gamma\text{-FeOOH}$ ).

TABLE III  
Evaluation of electron diffraction patterns of the intermediate products of oxidation of FeCl<sub>2</sub> at pH 7 in dependence on the oxidation time

2 min oxidation			3 min oxidation			4 min oxidation			5 min oxidation			10 min oxidation		
<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>	<i>d</i> nm	<i>I</i> %	phase <sup>a</sup>
0.299	5	GR	0.264	100	GR	0.330	70	L	0.327	60	L	0.323	30	L
0.257	100	GR	0.195	50	L	0.269	10	GR	0.245	50	L	0.245	20	L
0.212	50	GR	0.177	10	GR	0.248	30	L	0.193	90	L	0.233	30	L
0.181	15	GR	0.140	5	L	0.193	100	L	0.153	100	L	0.191	100	L
0.151	70	GR	0.159	100	L + GR	0.175	5	GR	0.139	10	L	0.154	100	L
			0.120	30	L	0.154	90	L + GR	0.120	20	L	0.139	20	L
						0.140	10	L				0.121	40	L
						0.121	20	L						

<sup>a</sup> GR = Green Rust, L = lepidocrocite ( $\gamma$ -FeOOH).



TABLE IV  
Characteristic bands in the infrared spectra of Green Rust

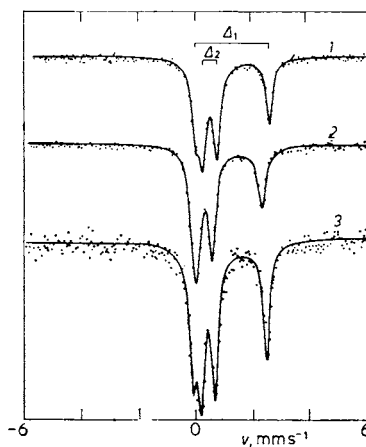
Anion in GR	Band position $\text{cm}^{-1}$				Anion electronegativity <sup>11</sup>
$\text{SO}_4^{2-}$	770	720	475	508	3.6
$\text{Cl}^-$	720	680	470	505	3.1
$\text{Br}^-$	685	620	470	500	2.9
$\text{I}^-$	642	460			2.6

TABLE V  
Parameters of Moessbauer spectra of iron(II) salt oxidation intermediates

Anion in GR	$\Delta_1$ doublet			$\Delta_2$ doublet		
	$IS^a$ $\text{mm s}^{-1}$	$Q^b$ $\text{mm s}^{-1}$	$I^c$ %	$IS$ $\text{mm s}^{-1}$	$Q$ $\text{mm s}^{-1}$	$I$ %
$\text{SO}_4^{2-}$	1.08	2.59	43.9	0.28	0.51	56.1
$\text{Cl}^-$	1.08	2.42	37.3	0.32	0.52	62.7
$\text{I}^-$	1.04	2.61	53.2	0.29	0.51	46.8

<sup>a</sup> Isomeric shift; <sup>b</sup> quadrupole splitting; <sup>c</sup> relative intensity of Moessbauer line.

FIG. 4  
Moessbauer spectra of GR substances ( $v$  is velocity). 1 GR- $\text{SO}_4$ , 2 GR- $\text{Cl}$ , 3 GR- $\text{I}$



on the anion, the shift to lower wavenumbers being correlatable<sup>11</sup> with decreasing electronegativity of the anions. Sulphate stretching vibrations at 1 000–1 200  $\text{cm}^{-1}$  are observable in the spectrum of GR-SO<sub>4</sub>. The vibrational band splitting revealed that the  $T_d$  symmetry of the SO<sub>4</sub> group is disturbed, the actual site symmetry of this anion in GR-SO<sub>4</sub> being  $C_{3v}$ . This suggests that one of the oxygen atoms is bonded in a way different from that of the others.

The infrared spectra of GR-Cl have been published by Misawa and coworkers<sup>3</sup>, who attributed the band pair at 670–800  $\text{cm}^{-1}$  to a skeletal vibration and the sharp band at 3 510  $\text{cm}^{-1}$  to the OH stretching vibration. The latter band was not observed in our spectra; it should be noted that this band position approaches closely those of the OH stretchings in alkali hydroxides, which actually may be present as impurities in imperfectly washed GR samples.

The Moessbauer spectra were measured for samples at the Fe<sup>II</sup>/Fe<sup>III</sup> ratio 1 : 1 (Fig. 4). They consist of two doublets at room temperature; the one,  $\Delta_1$  with the isomeric shift  $IS = 1.08 \text{ mm s}^{-1}$  and quadrupole splitting  $Q = 2.5 \text{ mm s}^{-1}$ , was attributed unambiguously to Fe<sup>2+</sup>, the other,  $\Delta_2$  ( $IS = 0.03 \text{ mm s}^{-1}$ ,  $Q = 0.51 \text{ mm} \cdot \text{s}^{-1}$ ), to Fe<sup>3+</sup> in octahedral coordination. The  $\Delta_1$  doublet is broad and actually can comprise several bands with slightly different splitting parameters. The splitting parameters are virtually independent of the anion involved (Table V). The valency states are resolved, electron exchange between Fe<sup>2+</sup> and Fe<sup>3+</sup> such as in magnetite does not occur in GR. At liquid nitrogen temperature,  $\Delta_2$  splits into two components, a doublet with parameters identical with those of  $\Delta_2$ , and a magnetically split component. This behaviour can be best explained in terms of superparamagnetism of the small GR particles. The character of our spectra is analogous to that of the published Moessbauer spectra of products of oxidation of iron(II) hydroxide<sup>11</sup>, our splitting values, however, are appreciably different.

#### REFERENCES

1. Feitknecht W., Kellner G.: *Z. Anorg. Allg. Chem.* 262, 61 (1950).
2. Bernal D., Dasgupta D. R., Mackay A. L.: *Clay Miner. Bull.* 4, 15 (1959).
3. Misawa T., Suétaka W., Shimodaira S.: *Bull. Chem. Soc. Jpn.* 42, 3339 (1969).
4. Derie R., Ghodsi M.: *Ind. Chem. Belg.* 37, 731 (1972).
5. Petit J. C.: *C. R. Acad. Sci A* 1960, 878.
6. Šolcová A., Šubrt J., Vinš J., Hanousek F., Zapletal V., Tláskal J.: *This Journal* 46, 3049 (1981).
7. Detournay J., de Miranda L., Derie R.: *Corros. Sci.* 15, 295 (1975).
8. Feitknecht W.: *Helv. Chim. Acta* 24, 676 (1941).
9. Allman R.: *Chimia* 24, 99 (1970).
10. Pritchard A. M., Mould B. T.: *Corros. Sci.* 11, 1 (1971).
11. Bacanov S. S.: *Elektronegativita prvku a chemická vazba*, p. 160. Published by SNTL — Nakladatelství technické literatury, Prague 1965.

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